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LIQUID DYING AGENTS

[Flüssige Farbmittel]

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Abstract

The invention concerns liquid dying agents that are characterized by the fact that they contain one or more dyes that are readily soluble in water or solvents, one or more pigments and solvents, and optionally dispersing agents.

The dying agents in accordance with the invention are highly suitable for coloring aqueous and non aqueous media, in particular, glues and shoe polishes.

The invention concerns liquid dying agents, which are characterized by the fact that they contain one or more soluble dyes, one or more finely divided pigments and solvents, and optionally dispersing agents.

Possibilities as readily soluble dyes are cationic, nonionic and anionic dyes, where ionic dyes as a rule are made readily soluble in the solvent that is used by means of suitable anions or cations.

Cationic dyes for the dying agents in accordance with the invention derive chiefly from the di- or triarylmethane, xanthene, azo, cyanine, azacyanine, methane, acridine, safranine, oxazine, induline or nigrosine dyes. Individual compounds are, for example, Basic Yellow 2 (C.I. 41000), Basic Red 1 (C.I. 45160), Basic Violet 10 (C.I. 45170), Basic Blue 26 (C.I. 44045), Basic Blue 7 (C.I. 42595), Basic Blue 1 (C.I. 42025), Basic Violet 1 (C.I. 42535), Basic Violet 3 (C.I. 42555), Basic Green 1 (C.I. 42040), Basic Green 4 (C.I. 42000) and phenazine dyes like Solvent Blue 7 (C.I. 50400). Dyes from the azo, triarylmethane and xanthene series are preferred.

Possibilities as anions for aqueous dying agents are the usual ones that derive from inorganic acids and lower carboxylic acids such as chloride, bromide, sulfate, methosulfate, ethosulfate, nitrate, formate, acetate or proprionate. If solubility in organic solvents is important, long-chain carboxylic acid anions like oleate are especially suitable.

The solubilizing anions can be introduced by reacting the cationic dyes in the form of the pertinent dye bases with the acids that provide the anions.

One may mention as dye bases, for example Solvent Yellow 34, (C.I. 41010:1), Solvent Orange 3 (C.I. 11270:1), Solvent Red 49 (C.I. 45170:1), Solvent Violet 8 (C.I. 42532:1), Solvent Violet 9 (C.I. 42555:1), Solvent Blue 2 (C.I. 42563:1), Solvent Blue 4 (C.I. 44045:1) and Solvent Black 7 (C.I. 50415:1).

Nonionic dyes for the dying agents in accordance with the invention chiefly derive from the azo, nitro or anthraquinone dyes, and the compounds listed in the Color Index under "solvent dyes" are to be mentioned especially.

In particular, sulfonic acid group-containing compounds from among the azo, anthraquinone, metal complex, triarylmethane or stilbene compounds are possibilities as anionic dyes, where azo dyes and phthalocyanine derivatives are especially preferred.

Individual anionic dyes are, for example, the dyes listed in the Color Index: Acid Yellow 3 (C.I. 47005), Acid Yellow 36 (C.I. 13065), Acid Yellow 19 (C.I. 18967), Acid Orange 7 (C.I. 15510), Acid Orange 8 (C.I. 15575), Acid Red 88 (C.I. 15620), Acid Red 351 (C.I. 28683), Acid Violet 90 (C.I. 18762), Acid Blue 9 (C.I. 42090), Acid Blue 193 (C.I. 15707), Direct Blue 86
(C.I. 74180) and

2,5-dichloro-4-sulfoaniline	→	3-cyano-4-methyl-2,6-di-(β-hydroxyethylamino)pyridine (as dibutylethanolamine salt)
2-hydroxy-3-nitro-5-sulfoaniline	→	1-phenyl-3-methylpyrazol-5-one (as chromium (1:2) complex)
2-hydroxy-4-sulfo-6-nitronaphthyl-1-amine	→	β-naphthol (as chromium (1:2) complex)
and		
2-hydroxy-3-sulfo-5-nitroaniline	→	1-phenyl-3-methylpyrazol-5-one (as chromium (1:2) complex)

One may mention in particular as cations that mediate water solubility alkali ($Li^{\oplus}$, $Na^{\oplus}$, $K^{\oplus}$), ammonium and substituted ammonium cations, especially alkanolammonium cations.

For dying agents in accordance with the invention that contain organic solvents, in particular the metal complex dyes are suitable as anionic dyes, for example the chromium or cobalt complexes of azo or azomethine dyes and copper phthalocyanine dyes.

In particular, longer-keeping [sic; longer-chain?] alkylammonium residues are suitable as cations for the dyes; the corresponding dyes are described, for example, in German Patent Nos. 12 26 727, 12 63 947 and 23 34 228.

A prerequisite for the ability of all of these dyes to be used in the dying agents in accordance with the invention is that they dissolve in a concentration that is as high as possible. The dyes can also be used in the form of concentrated dye solutions and methods for producing such solutions are described abundantly in particular in the patent literature, for example in the patent applications P 30 20 891.4, P 30 36 556.1, DE-AS [Auslegungsschrift patent application] 12 40 036, DE-AS 20 49 620, DE-OS [Offenlegungsschrift patent application] 22 28 260, DE-OS 28 52 863, DE-OS 28 16 506 or DE-AS 24 13 369 as in DE Patent [PS] No. 1 259 484 and DE-PS 2 334 228.

Inorganic and organic pigments are possibilities as pigments. The only prerequisite for the ability to use them is that they can be finely distributed in the dye agents. A representative choice of suitable pigments can be found in the chapter on pigments in the Color Index. Some preferred pigments and pigment groups are, for example: carbon black, iron oxides, phthalocyanines, azo pigments, nickel titanium yellow, chrome yellow, molybdate orange, Milori blue and quinacridone, perylene, oxazine and anthraquinoid pigments.

Inexpensive pigments like carbon black, iron oxides, azo compounds and phthalocyanines are preferred for economic reasons.

Practically all compounds that are usually used for the preparation of aqueous pigment dispersions are suitable as dispersion agents. Both anionic as well as cationic, but preferably nonionic, dispersion agents are possibilities. Suitable nonionic surfactants are, for example polyethylene glycols and ethoxylation products based on linear fatty acids, fatty amines, fatty acid amides and fatty alcohols. Suitable anionic dispersion agents are, for example fatty alcohol ether sulfates and alkylphenol ether sulfates. For example, quaternary ammonium salts of long chain fatty alkylamines can be used as cationic surfactants. However, if anionic or cationic surfactants are used, one must take care that reactions with the anionic or cationic dye are avoided.

The dying agents in accordance with the invention contain water and/or organic solvents.

The choice of the organic solvent or solvents for the dying agents in accordance with the invention is governed by the purpose of these dye agents. For example, flexographic inks normally contain polar solvents, while paints and wax solutions, on the other hand, contain nonpolar solvents.

Suitable as polar organic solvents are, for example, alkanols, glycols, glycol ethers, amides, tetrahydrofuran, butyrolacetone, dioxane, dimethylsulfoxide, lower carboxylic acid esters, ketones and aliphatic carboxylic acids, where, of these formic acid and acetic acid are preferred.

Possibilities as nonpolar and less polar organic solvents are long-chain aliphatic alkanols, carboxylic acids, esters, ketones or ethers and, preferably, aliphatic and aromatic hydrocarbons and halogen-substituted hydrocarbons.

The dying agents in accordance with the invention contain dyes and pigments in amounts of about 20-70%, preferably 40-60%. The ratio of the amounts of soluble dye to pigment can be varied in a wide range, with the determining factors in this case essentially being the desired color tone and economic factors. The amount of polar (including water) and/or nonpolar solvents is 30-80%, preferably 40-60%, with respect to the total amount. The amount of acids and surfactants that may be present can be up to 30%, preferably 5 to 20%.

The choice of dyes is, of course, likewise governed by the purpose and by the solubility in the given medium.

To produce the dying agents in accordance with the invention, the solution of a readily soluble dye in an organic solvent can, for example, be mixed with a preferably nonaqueous pigment dispersion. However, a pigment can also be directly dispersed into the dye solution. Of course, still other substances like thickeners or binders can be added to the dying agents in accordance with the invention. Details of the preparation can be learned from the examples, in which data concerning parts and percentages in each case refer to weight, unless otherwise noted.

The dying agents in accordance with the invention are suitable on the one hand for coloring aqueous media of all kinds, for example, paper pulps, glues, wood impregnation agents, pesticides, fertilizers, also for coloring and impregnating glass fibers and glass wool, jute felt, aqueous printing inks, mesh fabrics for carpet pads, and so forth. The dying agents in accordance with the invention that contain water are especially valuable for coloring glues, such as are used in the production of chipboard.

On the other hand, the dying agents in accordance with the invention are especially suitable for coloring media of all kinds that contain organic solvents, for example, bean masses, candles, printing inks, paints, wood impregnation agents, pesticides, adhesives, etc. The dying agents in accordance with the invention that contain organic solvents are especially valuable for coloring shoe polishes.

The dying agents in accordance with the invention offer economic advantages in particular over the previously used dyes. It was surprising above all that they can be prepared in homogeneous form and without demixing.

Example 1

2 parts of a liquid dye containing 40% C.I. Acid Orange 7 (C.I. 15510)

1 part of a pigment preparation containing 35% color black (C.I. Pigment Black 7) and nonionic dispersion agents and glycol,

is mixed while being stirred. A liquid, slightly thixotropic dying agent mixture with good storage stability is obtained.

Example 2

1 part of a liquid dye containing 45% C.I. Basic Violet 49 (preparation described in DE-OS 22 28 260, Example 3), and

1 part of a pigment preparation containing 40% iron oxide red (C.I. Pigment Red 101) and nonionic dispersion agents and glycol,

is mixed while being stirred. A readily flowing mixture that can easily be incorporated into aqueous media is obtained.

Example 3

2 parts of a liquid dye containing 45% C.I. Basic Violet 49 (see Example 2), and

1 part of a pigment preparation containing 60% iron oxide red (C.I. Pigment Red 101) and nonionic dispersion agents and dipropyleneglycol,

is mixed while being stirred. A readily flowing paste that is easily mixable with aqueous media is obtained.

Example 4

2 parts of a liquid dye containing 45% C.I. Basic Violet 49 (see Example 2), and

1 part of a pigment preparation containing 35% color black (C.I. Pigment Black 7) and nonionic dispersion agents and glycol,

is mixed while being stirred. A liquid dying agent mixture with good flowability and storage stability is obtained

Example 5

2 parts of a liquid dye containing 40% C.I. Acid Orange 7 (see Example 1), and

1 part of a pigment preparation containing 40% copper phthalocyanine blue (C.I. Pigment Blue 15:1) and nonionic dispersion agents and glycol,

is mixed while being stirred. The resulting storage-stable mixture can easily be mixed into aqueous media.

Example 6

200 parts of a liquid dye containing 40% C.I. Acid Orange 7 (see Example 1),

45 parts of a transparent iron oxide red (C.I. Pigment Red 101),

5 parts of an ethoxylated fatty alcohol,

20 parts ethylene glycol and

80 parts water,

is ground for one hour in an agitator ball mill. The resulting paste-like dying agent is storage-stable, free of specks and readily mixable with aqueous media.

Example 7

100 parts of a liquid dye containing 45% C.I. Basic Violet 49 (see Example 2),

120 parts of iron oxide red (C.I. Pigment Red 101),

5 parts of an ethoxylated fatty alcohol,
20 parts ethylene glycol and
40 parts water,
is ground for one hour on in agitator ball mill. A readily flowing paste that can easily be incorporated into aqueous media is obtained.

Example 8

100 parts of a liquid dye containing 45% C.I. Basic Violet 49 (see Example 2),
80 parts of a β-copper phthalocyanine blue (C.I. Pigment Blue 15:3),
5 parts of an ethoxylated fatty alcohol,
20 parts ethylene glycol and
80 parts water,
is mixed for one hour in an agitator ball mill. The resulting paste-like mixture is readily flowing and perfectly mixable with aqueous media.

Example 9

100 parts of an orange liquid dye (see Example 3, DE-OS 28 52 919),
80 parts of a β-copper phthalocyanine blue (C.I. Pigment Blue 15:3),
5 parts of an ethoxylated fatty alcohol,
20 parts ethylene glycol and
40 parts water,
is ground for one hour in an agitator ball mill. A readily flowing paste that can easily be incorporated into aqueous media is obtained.

Example 10

200 parts of a liquid dye containing 40% C.I. Acid Orange 7 (see Example 1),
250 parts iron oxide red (C.I. Pigment Red 101),
10 parts of a condensation product of β-naphthalenesulfonic acid and formaldehyde (as sodium salt),
20 parts ethylene glycol and
20 parts water,
is ground for one hour in an agitator ball mill. The resulting storage-stable paste is well suited for coloring aqueous media.

Example 11

100 parts of a liquid dye containing 45% C.I. Basic Violet 49 (see Example 2),

120 parts iron oxide red (C.I. Pigment Red 101),
5 parts C_{12}/C_{14}-fatty alkyldimethylbenzylammonium chloride,
20 parts ethylene glycol and
3 parts polyvinylpyrrolidone,

is ground for one hour in an agitator ball mill. A storage-stable, readily flowing paste that is highly compatible with aqueous media is obtained.

Example 12

10 parts of the pigment C.I. Pigment Blue 15:3, C.I. 74160 (β-copper phthalocyanine blue), is ground with 9 parts of a solution of a brown oxazine dye (70% in 2-ethylhexanol) in an agitator ball mill for one hour.

The brown dye was prepared by oxidation of 2-ethylhexyl-o-phenylenediamine and is described in the application P 30 20 891.4, Example 4.

A black readily flowing concentrate that is suitable for coloring shoe polish is obtained.

Example 13

20 parts of a pigment paste based on C.I. Pigment Blue 15:3 and 80 parts of a solution of a brown oxazine dye (corresponding to Example 12) are mixed while being stirred. One obtains a readily flowing black mixture that has good storage stability and that can easily be incorporated into naphtha*-containing wax mixtures.

The above pigment paste contains

25% C.I. Pigment Blue 15:3 (β-copper phthalocyanine blue),
15% dispersion agent and
60% of a solvent mixture of
7 parts of a high-boiling aromatic hydrocarbon mixture and
3 parts ethylene glycol acetate

Example 14

25 parts of a pigment paste of C.I. Pigment Blue 15:1, C.I. 74160 (α-copper phthalocyanine blue) in a short oil alkyd resin is mixed while stirring with 75 parts of a solution of a brown oxazine dye (corresponding to Example 12).

A liquid dying agent mixture with good flowability and storage stability that is very suitable, for example, for black shoe polish, is obtained.

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* [i.e., solvent]

Example 15

10 parts of the pigment C.I. Pigment Violet 27, C.I. 42535:3 (color lake of methyl violet) is mixed with 90 parts of a solution of a brown oxazine dye (corresponding to Example 12) for one hour in an agitator ball mill.

The resulting readily flowing dying agent is storage stable, free of specks and easily mixed with systems based on organic solvents.

Example 16

20 parts of the pigment C.I. Pigment Blue 27 (Milori blue) is mixed with 80 parts of a solution of a brown oxazine dye (corresponding to Example 12) for one hour in an agitator ball mill.

A readily flowing black mixture that is suitable, for example, for coloring shoe polish is obtained.

Example 17

15 parts of the pigment C.I. Pigment Yellow 12, C.I. 21090 (benzidine yellow) is ground with 85 parts of a solution of condensation products of 1,4-dihydroxyanthraquinone and 2,3-dihydro-1,4-diaminoanthraquinone with β-ethylhexoxypropylamine, β-ethylhexylamine and γ-methoxypropylamine for one hour in an agitator ball mill.

A thin dark green dying agent preparation that is miscible with organic solvents is obtained.

Example 18

20 parts of the pigment C.I. Pigment Yellow 42, C.I. 77492 (iron oxide yellow) is ground with 80 parts of a liquid dye concentrate for 30 minutes on an agitator ball mill. The liquid dye concentrate consists of a 50% solution of the azodye o-aminoazotoluene→β-phenylethylnaphth-2-ol (isomer mixture, described in DE-OS 28 52 863) in a mixture of aromatic hydrocarbons.

The resulting thin red dying agent mixture is highly storage stable, does not tend to flake or settle and is suitable for coloring media based on organic solvents.

Example 19

30 parts of a pigment paste that is based on C.I. Pigment Blue 15:3 (corresponding to Example 13) is mixed with 40 parts of a dye-based digestion of 40% C.I. Solvent Blue 4, C.I. 44045 (Victoria blue base B) in 60% olein and 30 parts toluene while stirring.

A low viscosity dye paste with good storage stability that can be used for coloring organic media of all kinds such as wax solutions, printing inks and paints, is obtained.

Example 20

10 parts of the pigment C.I. Pigment Blue 15:3 (β-copper phthalocyanine blue) is ground with 88 parts of a solution of a brown oxazine dye (corresponding to Example 12) and 2 parts of a vinylpyrrolidone-vinyl acetate copolymer for one hour in an agitator ball mill.

The resulting dying agent preparation is suitable for coloring alcohol flexographic inks. The inks produced therewith have a perfect sublimation fastness. This preparation can also be used for indelible ball point pen ink pastes, for example, according to the following recipe:

100 parts of the said black mixture
25 parts benzyl alcohol
25 parts phenylglycol
10 parts olein
5 parts 1,2-propyleneglycol
35 parts phthalate resin

Writing made with this ball point pen ink cannot be removed by water, ethanol, acetone or toluene.

Example 21

20 parts of a pigment paste based on C.I. Pigment Blue 15:3 (corresponding to Example 13) is mixed with 80 parts of a liquid dye of the following composition:

34% of the 1:2 cobalt-mixed complex of 4-nitro-2-aminophenol→1-phenyl-3-methylpyrazolone and 4-nitro-2-aminophenol→β-naphthol,
33% dimethylformamide and
33% butyldiglycol

A thin dying agent preparation that has good storage stability, does not tend to flake and that is suitable for coloring media of all kinds that are based on organic solvents is obtained.

Example 22

12 parts of a pigment paste based on C.I. Pigment Blue 15:3 (corresponding to Example 13) is mixed with 88 parts of a 60% solution of orange dye in a high-boiling aromatic hydrocarbon solvent while stirring. The preparation of the orange dye is described in DE-AS 24 34 110, Example 1.

The resulting low-viscosity brown dying agent can be stabilized by adding suitable thickeners such as colloidal silica. It is suitable, for example, for coloring shoe polish.

Example 23

50 parts of a yellow liquid dye (a) is mixed with 50 parts of a pigment paste (b) based on copper phthalocyanine blue, while stirring.

5 parts of this readily flowing mixture is stirred into 95 parts flexographic varnish (c). The resulting green flexographic ink can be easily printed and has good water-fastness.

The yellow liquid dye (a) is C.I. Basic Yellow 2 (C.I. 41000) in the form of the dodecylbenzene sulfonate, dissolved about 65% in a mixture of ethylene glycol and methyl isopropyl ketone.

The pigment paste (b) contains about 30% C.I. Pigment Blue 15:2, C.I. 74160, dispersed in a mixture of dodecylbenzenesulfonic acid, colophonium and toluene.

The flexographic varnish (c) contains

10% styrene-maleic acid mixed polymer

8% synthetic laking agent

82% ethanol/ethylene glycol (mixture 9:1)

Example 24

33 parts of a yellow liquid dye (a) and 67 parts of a pigment preparation (b) based on copper phthalocyanine blue are mixed with each other while being stirred.

5 parts of this mixture is stirred into 95 parts of an aqueous binder solution (c). A brilliant green flexographic ink that is suitable for printing paper, for example cement bags, is obtained.

The said yellow liquid dye (a) is the azo dye from flavonic acid (= 4,4-diaminostilbene-2,2-disulfonic acid), diazotized and coupled to phenol, as an approximately 25% solution in a mixture of neopentyl glycol and water.

The pigment preparation (b) contains about 40% C.I. Pigment Blue 15:1, dispersed in a mixture of nonionic dispersion agents, glycol and water.

The binder solution (c) contains an ester of phthalic acid and trimethylolpropane, saponified with ammonia and dissolved in a mixture of n-propanol and water as saponifiable resin.

Claims

1. Liquid dying agents containing one or more soluble dyes, one or more finely divided pigments and solvents and optionally dispersion agents.

2. Dying agents as in Claim 1, characterized by the fact that they contain anionic or cationic dyes as soluble dyes and water and/or water-soluble solvents and optionally organic acids as solvents.

3. Dying agents as in Claim 1, characterized by the fact that they contain dyes that are readily soluble in organic solvents as soluble dyes and organic solvents as solvents.

4. Dying agents as in Claims 1 and 2, characterized by the fact that they contain anionic azo dyes or phthalocyanine derivatives as soluble dyes.

5. Dying agents as in Claims 1 and 2, characterized by the fact that they contain cationic dyes of the azo, triarylmethane or xanthene series as soluble dyes.

6. Dying agents as in Claims 1 and 3, characterized by the fact that they contain nonionic compounds from the series of the solvent dyes or cationic or anionic dyes made soluble in organic solvents by appropriate anions or cations, as soluble dyes.

7. Dying agents as in Claims 1 and 2, characterized by the fact that they contain carbon black, iron oxides, azo compounds or phthalocyanines as pigments.